PURIFICATION OF THE MULTIWALLED CARBON NANOTUBES (MWCNTs) AND THE APPLICATION OF THE 3R (REDUCE, REUSE AND RECYCLE) CONCEPT ON THE CHITOSAN/MWCNTs NANOCOMPOSITES

CHENG YOKE KOOI

UNIVERSITI SAINS MALAYSIA

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By

CHENG YOKE KOOI

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LIST OF ABBREVIATIONS

3R	Reduce, reuse and recycle
Abs	Absorbance
Al	Aluminium
Al_2O_3	alumina
AlO_2^-	aluminate ions
Ar	Argon
ATR	Attenuated total reflectance
CH_3CH_2OH	Ethanol
Cl_2	Chlorine
CNTs	Carbon nanotubes
Co	Cobalt
CVD	Chemical vapor deposition
DNS	2-hydroxy-3,5-dinitrobenzoic acid
DWCNTs	Double-walled carbon nanotubes
E	Young modulus
EDS	Energy dispersive spectroscopy
Fe	Iron
FE-SEM	Field emission scanning electron microscopy
Fig	Figure
FTIR	Fourier transformation infra-red
Gel/MMT-CS	Gelatin/montmorillonite-chitosan
GlcN	D-glucosamine
GlcNAc	N-acetylglucosamine
GPa	Gigapascal
GPO	Gas phase oxidation
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HNO_3	Nitric acid
J/cm^2	Joules per square centimeter
kDa	Kilodaltons

kHz	Kilohertz
$KMnO_4$	Potassium permanganate
KOH	Potassium hydroxide
LCA	Life-cycle assessment
LPO	Liquid phase oxidation
Mo	Molybdenum
Mw	Molecular weight
MWCNTs	Multiwalled carbon nanotubes
NaAc	Sodium Acetate
Na-K tartarate	Rochelle salts
NaOH	Sodium hydroxide
NH_3	Ammonia gas
Ni	Nickel
nm	Nanometer
ns	Nanosecond
$NTANa_3$	Nitrilotriacetic acid trisodium salt monohydrate
PACl	Polyacryloyl chloride
Pd	Palladium
PMMA	Poly(methyl methacrylate)
PS-g-(GMA-co-St)	Polystyrene-g-(glycidyl methacrylate-co-styrene)
Pt	Platinum
r.p.m	Revolutions per minute
S/cm	Siemens per centimeter
SEM	Scanning electron microscopy
SWCNTs	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TPa	Terapascal
TS	Tensile strength
U/ml	Units per milliliter

LIST OF SYMBOLS

α	Alpha
β	Beta
ε	The elongation at break
η	Recovery efficiency of the MWCNTs
π	Pi bond

PENULENAN NANOTIUB KARBON DINDING BERLAPIS (MWCNTs) DAN APLIKASI KONSEP 3R (MENGURANG, GUNA SEMULA DAN KITAR SEMULA) BAGI KITOSAN/MWCNTs NANOKOMPOSIT

ABSTRAK

Nanotiub karbon dinding berlapis yang disediakan mengandungi bendasing seperti karbon amorfus, pemangkin logam dan sokongan pemangkin yang menjejaskan pengunaan MWCNTs. Kombinasi etsa basah (0.2 M natrium sitrat, 0.2 M $NTANa_3$ dan 0.1 M NaOH dalam nisbah isipadu 2:2:1) berjaya menyingkirkan kandungan bendasing daripada nanotiub karbon dinding berlapis (MWCNTs) mentah. Suhu rawatan merupakan faktor utama bagi keberkesanan etsa basah dalam penyingkiran bendasing daripada MWCNTs mentah manakala ia tidak dipengaruhi oleh masa tindak balas yang diambil. Bendasing utama, iaitu alumina telah dikurangkan daripada 24.0 berat % kepada 9.3 berat % manakala cobalt dan molybdenum masing-masing telah dikurangkan daripada 9.6 berat % kepada 4.4 berat % dan 2.3 berat % kepada 0.6 berat % pada suhu rawatan, 138^{o}C. Rawatan lanjutan dengan akueous piranha mengurangkan alumina kepada 6.7 berat % dan pemangkin logam kepada 0.7 berat % cobalt dan 0.1 berat % molybdenum. Walaupun MWCNTs mampu diguna sebagai fiber untuk meningkatkan sifat-sifat mekanik atas polimer tetapi ia berbahaya pada manusia. Jadi, konsep 3R digunakan untuk mengatasi kekurangan MWCNTs. Nanokomposit kitosan/MWCNTs ini disediakan melalui kaedah pemprosesan larutan. Peningkatan kadar pengeringan

nanokomposit kitosan/MWCNTs mengakibatkan peningkatan dalam kekuatan tegangan (TS) dan Young Modulus (E) nanokomposit tetapi mengurangkan had putus pemanjangan (ε) nanokomposit. Nanokomposit kitosan/MWCNTs mencapai Young Modulus tertinggi apabila amaun MWCNTs adalah 0.1 berat %. Walaubagaimanapun, TS dan E nanokomposit kitosan/MWCNTs menurun secara mendadak apabila amaun MWCNTs melebihi 0.1 berat %. Penyerapan air dan biodegradasi nanokomposit dikaji berdasarkan filem kitosan dan nanokomposit kitosan/MWCNTs yang dikeringkan melalui proses pemanasan. Amaun MWCNTs cenderung mengurangkan penyerapan air dan kadar degradasi nanokomposit dalam larutan buffer natrium asetat. Nanokomposit kitosan/MWCNTs yang direndam dalam larutan degradasi mengalami kehilangan secara seluruh dalam masa 3 jam. Produk degradasi daripada kitosan iaitu glukosamina (GlcN) telah meningkat 33 dan 131 kali ganda bagi filem kitosan dan nanokomposit kitosan/MWCNTs masing-masing apabila kepekatan larutan buffer natrium asetat meningkat kepada 0.1 M. Kadar degradasi filem kitosan dalam larutan buffer natrium asetat dipercepatkan 49.8 % dengan penambahan pepsin. Kecekapan pemulihan MWCNTs melalui pemisahan fizikal asas adalah sebanyak 89.7 %. Data yang diperolehi daripada thermogravimetric analisis (TGA), imbasan mikroskop elektron (SEM) dan ujian tegangan membuktikan bahawa MWCNTs yang dipulihkan daripada proses degradasi nanokomposit mempunyai sifat-sifat yang seiras dengan MWCNTs asal. Penemuan ini menunjukkan bahawa selepas penggunaan kitosan/MWCNTs nanocomposite, MWCNTs boleh diguna dan dikitar semula tanpa membawa kesan sampingan kepada alam sekitar.

PURIFICATION OF THE MULTIWALLED CARBON NANOTUBES (MWCNTs) AND THE APPLICATION OF THE 3R (REDUCE, REUSE AND RECYCLE) CONCEPT ON THE CHITOSAN/MWCNTs NANOCOMPOSITES

ABSTRACT

The as-prepared multiwalled carbon nanotubes (MWCNTs) consist of high impurities of amorphous carbon, metal catalysts and catalyst support that impeded the MWCNTs applications. The combination of the wet etchant (0.2 M sodium citrate, 0.2 M $NTANa_3$ and 0.1 M NaOH, in the volumetric ratio of 2:2:1) was used to remove the amount of impurities of the raw MWCNTs. Treatment temperature was the key factor for the effectiveness of the wet etchant on the removal of residue but it was not affected by the reaction time. Alumina, the major impurity was reduced from 24.0 wt. % to 9.3 wt. % whereas cobalt and molybdenum were reduced from 9.6 wt. % to 4.4 wt. % and 2.3 wt. % to 0.6 wt. %, respectively at temperature of 138^{o}C in wet etchant treatment. With the aid of the piranha solution treatment, further reduced the impurities; alumina to 6.7 wt. %, cobalt to 0.7 wt. % and molybdenum to 0.1 wt. %. Although MWCNTs able to act as fiber to enhance mechanical properties of the polymer but they are harmful to the living. Hence, The 3R conceptual idea is used to overcome the limitation of the MWCNTs. The chitosan/MWCNTs nanocomposites were prepared by solution processing method. Increasing of drying rates of the chitosan/MWCNTs nanocomposites led to the increase in their tensile strength (TS) and Young's Modulus (E) but decreased their

elongation at break (ε). The chitosan/MWCNTs nanocomposites obtained the highest Young modulus when the loading of MWCNTs was 0.1 wt. %. However, the TS and E of the chitosan/MWCNTs nanocomposites decreased dramatically when the loading of MWCNTs was higher than 0.1 wt. %. The water absorption and biodegradation studies were conducted by using heated chitosan film and chitosan/MWCNTs nanocomposites. The loading of MWCNTs in chitosan/MWCNTs nanocomposites tend to reduce the nanocomposites' water absorption and their degradation rate in sodium citrate (NaAc) buffer. A complete disappearance of the chitosan/MWCNTs nanocomposites in the degradation solution was achieved within 3 h. The degraded product; glucosamine (GlcN) was increased 33 and 131 fold correspondingly to heated chitosan film and chitosan/MWCNTs nanocomposites when buffer concentration was increased from 0 to 0.1 M. Degradation of chitosan film in NaAc buffer solution was accelerated 49.8 % with the presence of pepsin. The recovery efficiency of MWCNTs by physical base separation reached at 89.7 %. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and tensile test results showed that the properties of the recovered MWCNTs were similar to the oxidized MWCNTs. This suggests that at the end of the usage of nanocomposite, the MWCNTs could be reused and recycled without releasing into environment.

CHAPTER 1

INTRODUCTION

1.1 Introduction of the Synthetic and Biodegradable Polymers

The synthetic polymers from non-renewable sources have been widely used for packaging, agriculture, building materials, hygiene products and other perishable commodities. They are resistance to chemical peroxidation and microbial degradation (Inoue et al., 1998; Kolybaba et al., 2003; Vroman and Tighzert, 2009). The non-renewable polymers have led to waste disposal problems and serious environmental pollution as they are non-biodegradable (Okada, 2002). The development of environmental friendly biodegradable polymers has been stimulated to substitute synthetic polymers because of the increasing of oil price and the concern of conserving the ecological system (Inoue et al., 1998; Okada, 2002; Vroman and Tighzert, 2009).

Biodegradable polymers are first introduced in the 1980s and they are forecasted to be expanded in the global market at an average annual rate of 13 %, starting from 2009 to 2014 (Michael et al., 2010; Vroman and Tighzert, 2009). They can be classified into two major categories based on their origin, which are synthetic biodegradable polymers and natural biodegradable polymers (Isabelle and Lan, 2009). Synthetic biodegradable polymers are chemically synthesized from renewable sources such as gelatin-g-poly(ethyl acrylate), N-carboxymethylchitosan and N-carboxybutylchitosan; and non-renewable sources, for example saturated aliphatic polyesters (polylactic acid, polyglycolic acid, polycaprolactone), polyhydroxyalkanoates (polyhydroxybutyrate, polyhydroxyoctanoate), polypropylene fumarate, vinyl polymers and aromatic copolyesters. On the other

hand, natural biodegradable polymers are produced by biological systems, such as polysaccharides (starch, cellulose, alginate, chitin/chitosan, hyaluronic acid derivatives), proteins (soy, collagen, fibrin gels, silk) and polynucleotides/nucleic acids which are available in large quantities from renewable sources. (Armentano et al., 2010; Chandra and Rustgi, 1998; Sabir et al., 2009)

Biodegradable polymers can be degraded and catabolized by microorganisms under natural environment to form carbon dioxide and water via oxidation, hydrolysis, photodegradation, thermodegradation, chemodegradation, abiotic or biotic reactions; followed by bioassimilation of the polymer fragments (Chandra and Rustgi, 1998; Lucas et al., 2008; Scott, 2000). Its biodegradability depends on its nature and the environment, such as neutral or slightly acidic and the degradation temperature usually falls within $20^{o}C$ and $60^{o}C$ for active microorganisms (fungi, bacteria, actinomycetes, etc) (Aminabhavi et al., 1990; Huang et al., 1990; Scott, 1999).

Life-cycle assessment (LCA) of materials provides a useful comparison of the ecological impact of comparable products. A simple example for the life cycle of natural biodegradable polymer is given in Figure 1.1. The natural biodegradable polymers were underwent biodegradable polymer processing and synthesis/modification in order to produce the finished products. The biowaste products were collected and then used as the biomass, humic matter or compost.

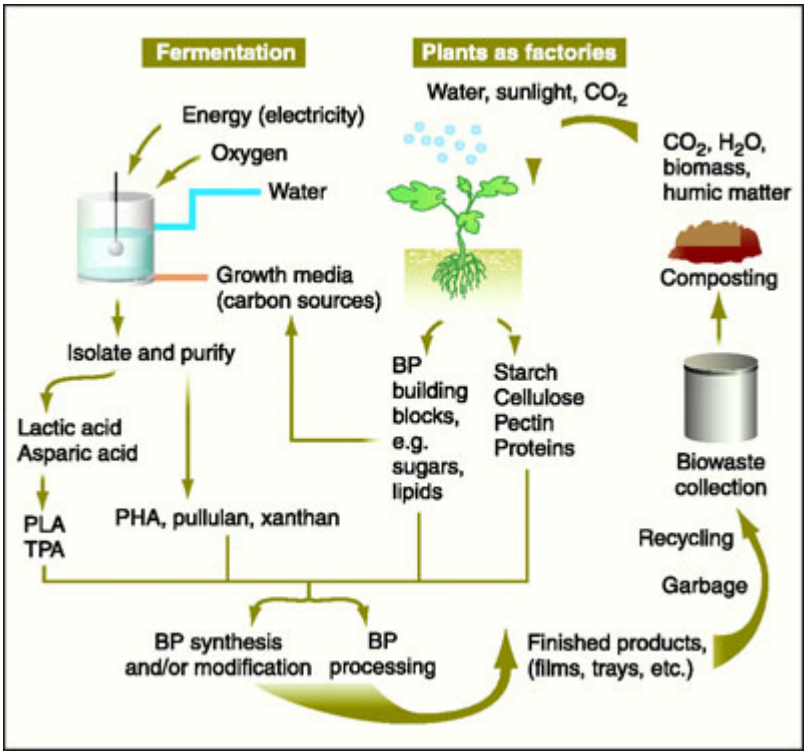


Figure 1.1. Life cycle of natural biodegradable polymers (Gross and Kalra, 2002)

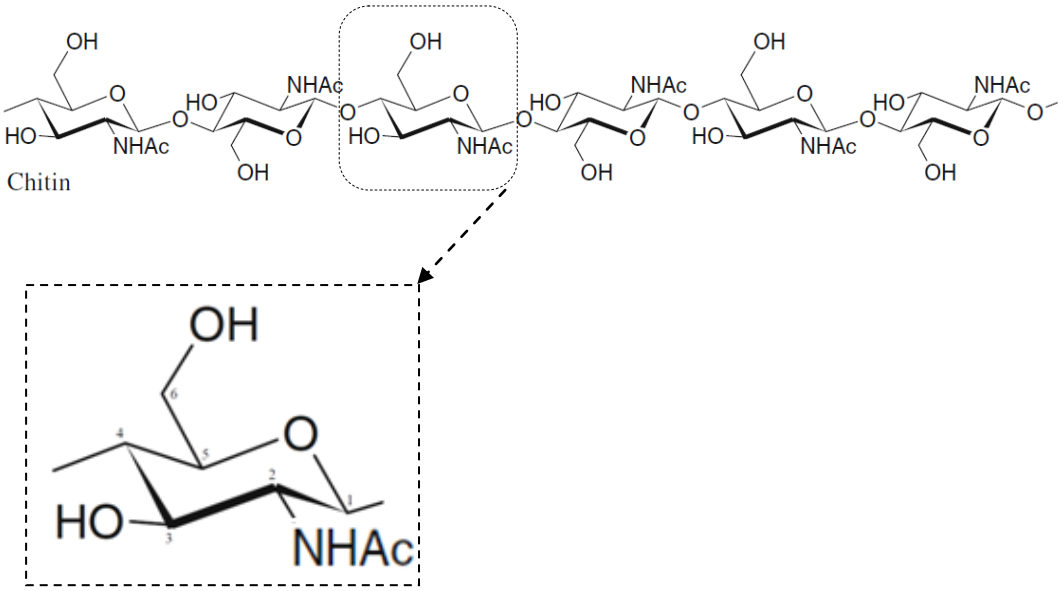
1.2 Chitin and Chitosan

Chitin, poly (β-(1→4)-N-acetyl-D-glucosamine), as shown in Figure 1.2 (a) is the most abundant natural polysaccharide after cellulose, available to the extent of over 10 gigatons (Harish Prashanth and Tharanathan, 2007). Chitin is found in many living organisms where it serves in many functions. It acts as a main structural component in the exoskeleton of arthropods or in the cell walls of fungi and yeast (Shahidi et al., 1999). The main commercial sources of chitin are crab and shrimp shells (Johnson and Peniston, 1982; Muzzarelli, 1977).

In industrial processing, chitin is extracted from crustaceans by acid treatment in order to dissolve the calcium carbonate content. Then, alkaline extraction was applied for protein solubilization and finally, decolorization agent was added to remove the residue pigments within the compound in order to get a colorless product (Rinaudo, 2006). Chitin can be named as chitosan when the degree

of deacetylation reaches about 50 % (Khor and Lim, 2003).

(a)



(b)

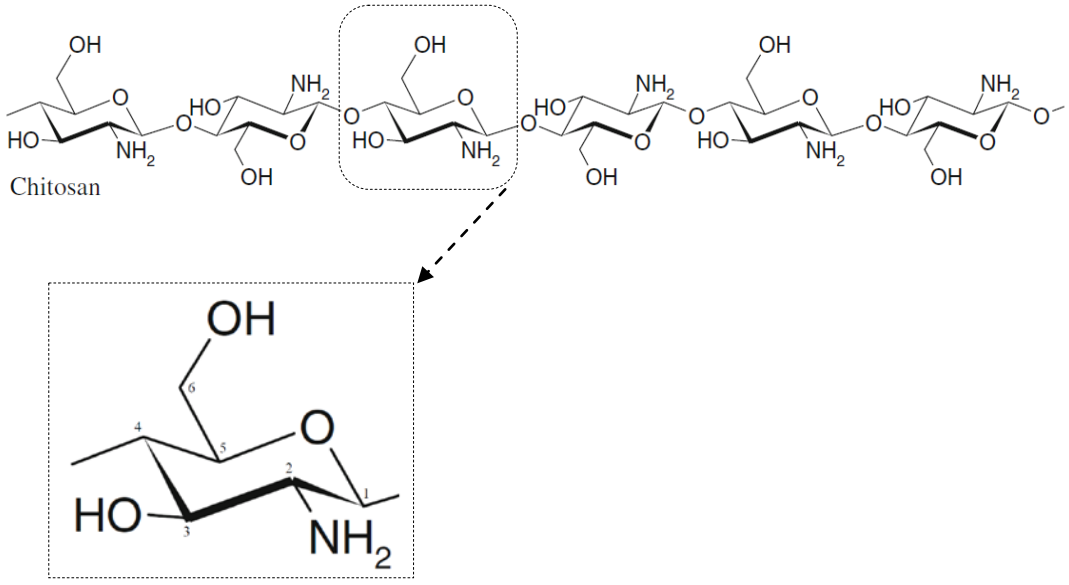


Figure 1.2. (a) Structure of chitin, (b) Structure of chitosan (Honarkar and Barikani, 2009)

Chitosan, is a linear heterocopolymer with molecular weight of 10,000 to 1 million Dalton (Pillai et al., 2009), composed of randomly distributed D-glucosamine (GlcN) and N-acetylglucosamine (GlcNAc) linked by β-1,4 glycosidic linkages (Ren et al., 2005), as shown in Figure 1.2 (b). Chitosan is a partially deacetylated polymer obtained from homogeneous or heterogenous alkaline deacetylation of chitin (Kurita et al., 1977). The degree of deacetylation is the ratio of N-deacetylated (amino) groups to N-acetyl groups at the C2 position in the backbone, as given in Figure 1.2. Physicochemical and biological properties of chitosan, for example crystallinity, solubility and biodegradability are dependent on degree of deacetylation. (Nam et al., 2010)

The rate of chitosan biodegradability is decreasing with respect to degree of deacetylation (Xu et al., 1996; Yang et al., 2007). In terms of the cystallinity, chitin (0 % deacetylated) and fully deacetylated (100 %) chitosan are having maximal crystallinity, whereas minimal crystallinity is obtained at intermediate degree of the deacetylation. In general, chitosan exist in the form lower than 100 % of deacetylated form thus, it is considered as a semi-crystalline (Senel and McClure, 2004). The solubility of chitosan in aqueous acidic media is directly proportional to the degree of deacetylation. Its solubilization occurs via protonation of the amino functional group on the C2 position of the GlcN repeating unit and favour the conversion of the polysaccharide to a polyelectrolyte in acidic media (Honarkar and Barikani, 2009). Furthermore, the free amino and hydroxyl groups in chitosan provide an important properties, for instance antibacterial, protein affinity, heavy metal chelation, reactivity and processability.

Chitosan is a unique pseudo-natural cationic polymer having excellent properties (Rinaudo, 2006) and thus has a wide range of applications in different fields, such as water and wastewater treatment, agriculture, fabric and textiles, cosmetics, nutritional enhancement and food processing (Harish Prashanth and Tharanathan, 2007; Shahidi et al., 1999). Its intrinsic characteristics like biodegradability, non-toxicity, bioactivity and biocompatibility make it a notable material, especially for pharmaceutical and biomedical fields (Jayakumar et al., 2010). The principal applications of chitosan in different fields have been summarized in Table 1.1.

1.3 Reduce, Reuse and Recycle (3R)

The rapid development of technology worldwide has significantly improved the living standards of people, but it has resulted in serious disruption to ecosystem and environment. High awareness has been highlighted on the effect of the carbon nanotubes (CNTs) towards environment due to its high toxicity and recent massive production.

The 3R (reduce, reuse and recycle) concept has been proposed with the aim to conserve resources by producing less hazardous waste. It promotes ecological balance through conscious behaviour and hence leads to saving of resources and energy. The CNTs are believed to be stable materials where their physical and chemical properties remain unchanged in most of the situations. Hence, 3R concept can be easily applied on the CNTs composites.

Table 1.1. Principal applications of chitosan in different fields (Rinaudo, 2006)

Field	Application
Biomedical	Surgical sutures and artificial skin
	Dental implants and rebuilding of bone
	Tissue engineering and encapsulating material
	Corneal contact lenses
	Time release drugs for animals and humans
Agriculture	Defensive mechanism in plants
	Stimulation of plant growth
	Seed coating, Frost protection
	Time release of fertilizers and nutrients into the soil
	Biosensors and surface conditionars
Water & waste treatment	Flocculant to clarify water (drinking water, pools)
	Ecological polymer for the removal of dyes, metal ions, and proteins and reduce odors
	Heavy metal-ion sensors
Food & beverages	Food packaging
	Bind lipids (reduce cholesterol)
	Preservative
	Thickener and stabilizer for sauces
	Protective, fungistatic, antibacterial coating for fruit
Cosmetics & toiletries	Maintain skin moisture
	Treat acne and tone skin
	Improve suppleness of hair
	Reduce static electricity in hair
	Oral care (toothpaste, chewing gum)
Biopharmaceutics	Immunologic, antitumoral
	Hemostatic and anticoagulant
	Healing, bacteriostatic

Reduce is referred to waste minimization that involves the process and the policy to minimize resources and energy used during manufacturing. The waste of the CNTs can be reduced by recovering the CNTs from the waste that contains of CNTs. This idea can be applied in most of the biodegradable polymer/CNTs nanocomposites, as well as other CNTs products. The global production of CNTs could be reduced if the recovered CNTs can be reused.

An item that has been used for more than once for the same function is called as reuse. CNTs are practically stable, insoluble and non-biodegradable fibers therefore the recovered CNTs were potentially considered to have high reusability value. Their unchanged physical and chemical properties are the key factors to ensure that the properties of the final product which made from recovered CNTs are comparable with those made from new synthesized CNTs. The reusable CNTs can be used to replace the single used fibers and hence, reduce the production of the CNTs. Thus, resulted in energy and resources savings.

Recycle is the process of separating, collecting and remanufacturing or converting waste into new products. The aim of the recycle is to reduce the consumption of fresh raw materials, energy usage, air and water pollution. The recovered CNTs can be used for recycle purposes where they can be incorporated into new products. Different from the reuse principle, the recovered CNTs might have the same or different role for the properties enhancement of the new product.

1.4 Problem Statement

CNTs produced by different synthesis methods usually contain significant amount of impurities, such as metal catalysts, catalyst supports or amorphous carbon. These impurities could lead to serious impediment on the CNTs applications. Based

on the previous studies (Porro et al., 2007; Shirazi et al., 2011; Song and Fang, 2007; Wang et al., 2006), most of the researchers concentrated on the metal catalysts and carbonaceous materials removal instead of the catalyst support removal, such as alumina.

The liquid phase oxidation (LPO) method was used to purify the as-prepared MWCNTs instead of the gas phase oxidation (GPO) since there will be a significant loss of CNTs in GPO, as compared to LPO. The metal impurities will be easily removed by acid treatment. Alumina support existed as minor impurities was usually removed by potassium hydroxide (KOH) (Louis et al., 2005) and sodium hydroxide (NaOH) (Qiu et al., 2005). A better reagent for removing alumina is needed because high amount of alumina was found exist in the chemical vapor deposition (CVD) MWCNTs, produced using alumina supports.

Biodegradable polymer, such as chitosan was proposed to be used as a substitution for conventional synthetic polymer to overcome the waste disposal problems and environmental issues. Unfortunately, the poor mechanical properties of chitosan had narrowed its applications. CNTs, which have remarkable tensile strength will be incorporated into chitosan in order to improve the mechanical properties of the resulted nanocomposites.

Although CNTs are useful with its remarkable properties, but its toxicity has raised high awareness in society (Bowman and Fitzharris, 2007; Donaldson et al., 2006; Maynard et al., 2011). The potential risk of CNTs had become even worse since it has been commercialized and produced in large amount. Hence, the conceptual idea of 3R is suggested in order to overcome the issue.

The present work focused on the purification of MWCNTs, application of MWCNTs in biodegradable polymer, reusability of the MWCNTs and its recycling efficiency. The biodegradation of chitosan/MWCNTs nanocomposites will be studied in order to reveal the effects of MWCNTs on their biodegradation ability. An enzyme solution is used to degrade the chitosan/MWCNTs nanocomposites, followed by physical based separation to recover the used MWCNTs.

1.5 Research Objectives

i. To remove the alumina supports, cobalt and molybdenum from the in-house synthesized MWCNTs.

ii. To prepare the chitosan/MWCNTs nanocomposites and study of their biodegradable properties.

iii. To recover the oxidized MWCNTs from the biodegradable nanocomposites and to investigate their reusability performance.

1.6 Scope of the Study

This research study consists of 4 major sections. The first section of the study is to select the most suitable purification method and reactants to purify as-prepared MWCNTs that synthesized from the CVD process. The effects of the parameters on the removal of alumina, such as reaction time, treatment temperature and reactants' concentrations were studied in order to determine the process variables that are significantly affecting the removal of impurities. The purified MWCNTs were characterized by thermogravimetric analysis (TGA), field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM).

Secondly, the process study was carried out to investigate the potential application of MWCNTs on the biodegradable chitosan/MWCNTs nanocomposites. Tensile test was used to examine the mechanical properties of chitosan/MWCNTs nanocomposites. The effect of weight percentages (wt. %) of MWCNTs, drying temperature and types of MWCNTs on the mechanical properties of chitosan/MWCNTs nanocomposites was studied to identify the chitosan/MWCNTs nanocomposites with the optimum mechanical properties.

Thirdly, the investigation was followed by biodegradation of chitosan film and chitosan/MWCNTs nanocomposites, using sodium acetate (NaAc) buffer solution containing pepsin enzyme. The effect of the type of solutions, concentration of NaAc buffer, wt. % of MWCNTs, as well as the types of the MWCNTs on the biodegradation rate of chitosan/MWCNTs nanocomposites were studied. The process conditions for optimum rate of chitosan/MWCNTs nanocomposites biodegradation were then used to recover MWCNTs. The biodegradation rate of the chitosan/MWCNTs nanocomposites was characterized by 2-hydroxy-3,5-dinitrobenzoic acid (DNS) colorimetric quantification and also qualitatively using a digital camera visualization.

Fourthly, the MWCNTs and mixture of chitosan were physically separated by centrifugation and filtration. The recovered MWCNTs were then collected and MWCNT recovery efficiency was determined. The recovered MWCNTs were then characterized by TGA and SEM in order to investigate their reusability. Moreover, the recovered MWCNTs were reused to fabricate chitosan/recovered MWCNTs nanocomposites. Lastly, the tensile test comparison between the chitosan/MWCNTs nanocomposites fabricated from oxidized MWCNTs and the recovered MWCNTs was used in order to verify the MWCNTs reusability.

1.7 Organization of the Thesis

This thesis consists of 5 chapters. Chapter one provides an outline of the overall research study, covering introduction of the synthetic and biodegradable polymers, chitin and chitosan, as well as the 3R concept. Problem statement was highlighted after reviewing the existing limitations faced in the purification of MWCNTs and the potential hazardous behaviour of the MWCNTs. The objectives were then formulated to address the encountered limitations. Finally, the organization of the thesis highlights the content of each chapter.

Chapter two presents an overall review of various research studies reported in the literature in this research area. This chapter begins with a brief introduction of CNTs, CNTs synthesis methods and their properties. Then, research studies related to the purification of CNTs, such LPO and GPO were reviewed. In addition, the hazardous of CNTs, CNTs functionlization, chitosan/CNTs nanocomposites fabrication methods and chitosan biodegradation were also reported.

Experimental materials and methodology were discussed in chapter three. The detailed information on the experimental methods was reported and the overview of the research study was illustrated in a flowchart diagram. The information on the materials, chemicals and equipments used in this research study were also given. Last but not least, the related equations for data analysis were presented in this chapter.

Chapter four is the most important chapter throughout the thesis. The detail information of the results and discussions were presented in this chapter. This chapter was arranged into four sections, accordingly to the stages of the research study. First section of this chapter presented the characterization outcome of the raw MWCNTs and purified MWCNTs. The effect of different process parameters on the

mechanical properties of the chitosan/MWCNTs nanocomposites were clearly reported in section two. Section three discusses the biodegradation behaviour of the chitosan/MWCNTs nanocomposites. Lastly, section four focuses on the MWCNTs recover efficiency and also their reusability.

Chapter five summarized the outcome of this research study. The conclusion of the research study was made based on the results and discussions. Besides, some recommendations and suggestions for future studies related to this research study were also given.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Carbon Nanotubes

A significant development in the area of nanotechnology has been made in the past decade. The discovery of carbon nanotubes (CNTs) has opened up new fields of study in physics, chemistry and materials science for their fundamental properties and potential applications.

CNTs, built from sp^2 carbon units, consist of honeycomb lattices and are seamless structure which were first reported by Iijima (1991) and Bethune et al. (1993). CNTs are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio of up to 28,000,000:1 (Zheng et al., 2004). CNTs can be found either as individual cylinders, single-walled carbon nanotubes (SWCNTs), two concentric cylinders, double-walled carbon nanotubes (DWCNTs) (Dai et al., 1996) or more concentric cylinders, multiwalled carbon nanotubes (MWCNTs). (Iijima, 1991)

It can be considered as single sheets of graphene, rolled into a cylindrical shape with axial symmetry and diameters between 0.7 and 10 nm. The way the wrapped-graphene sheet is represented by a pair of indices (n, m) called the chiral vector, where n and m denote the chiral indices and chiral angle θ, which is the angle between $\boldsymbol{C}_h$ and the nearest zigzag of C–C bonds, as shown in Figure 2.1 (a). The chiral vector of the rolled-up graphene is expressed in equation (2.1) (Kis and Zettl, 2008).

$$\boldsymbol{C}_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2 \equiv (n, m) \tag{2.1}$$

Different tubes have angles, θ between zero and 30°. Special tube types are armchair tubes (*n*, *n*) (θ = 30°) and zigzag tubes (*n*, 0) (θ = 0°) whereas other types of the tubes are considered as chiral tubes (*n*, *m*) (0 < θ < 30°), as shown in Figure 2.1 (b). (Popov, 2004)

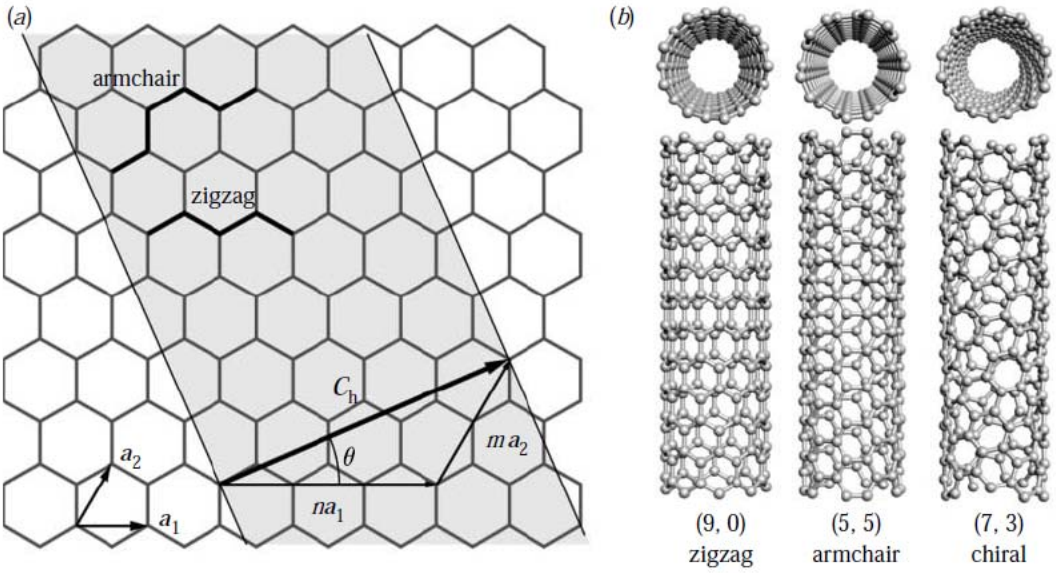


Figure 2.1. (a) Schematic of nanotube formation by 'rolling-up' a graphene sheet, (b) Models of zigzag, armchair and chiral nanotubes (Kis and Zettl, 2008)

2.2 CNTs Synthesis Method

Extensive research studies on CNTs synthesis, including electric arc discharge (Journet et al., 1997), laser ablation (Thess et al., 1996) and chemical vapour deposition (CVD) (Endo et al., 1995) have been carried out to produce bulk quantities of CNTs in order to fully exploit the CNTs technological potential (Moisala, 2006).

Electric arc discharge requires an extremely simple equipment and can be run in open air under certain condition (Veld et al., 2003). It involved the condensation of carbon atoms generated from vapourization of graphite targets. The operating temperature is close to the melting temperature of graphite, 3000-4000°C

(Dresselhaus et al., 2001). Arc discharge production process has an ability to produce SWCNTs with the aid of catalyst, such as Fe, Co or Ni (Bethune et al., 1993). On the other hand, MWCNTs are produced without the presence of catalyst and DWCNTs are produced selectively (Kushnir, 2007).

Laser ablation operates at similar condition to arc discharge from a system perspective except that a laser beam is focused onto the graphite and catalyst target. The energy for the laser also come from electricity (Dresselhaus et al., 2001; Kushnir, 2007). Kuo et al. (2001) reported that the synthesis of the small diameter MWCNTs required a high energy laser pulses (193 nm, 5 J/cm^2 and 20 ns duration time) to re-excite the carbon species contained in the laser ejected plume.

CVD involves the decomposition of hydrocarbon gases (e.g. methane, benzene, acetylene, naphthalene, ethylene, etc) as carbon feedstock over metal catalyst particles (e.g. Co, Ni, Fe, Pt or Pd) that are deposited at predefined locations on a substrate (Corrias et al., 2003; Ren et al., 1998). In the CVD process, SWCNTs are produced at higher temperatures with supported metal catalysts while MWCNTs could be formed at lower temperatures either with or without a metal catalyst (Qingwen et al., 2002).

2.3 Properties of the CNTs

CNTs are unique nanostructures which are known to have remarkable mechanical, chemical, thermal, electronic, adsorption and optical properties, making them interesting for various applications (Suzuki et al., 2007). The CNTs unique properties mainly depend on its structural conformation and hybridization state (Ajayan, 1999).

The chirality of the graphene sheet determines the electrical conductivity of the CNTs, giving rise to a wide variety of electronic applications (Hamada et al., 1992). The electronic capabilities possessed by CNTs are seen to arise predominately from interlayer interactions (Paradise and Goswami, 2007). Electrical current carrying capacity of the CNTs is 1000 times higher than that of copper wires (Collins and Avouris, 2000). CNTs electronic properties can be either metallic or semiconductor, depending on the their tubule diameter and chiral angle (Hamada et al., 1992; Saito et al., 1992). The early studies proved that metallic conduction can be achieved without the introduction of any doping effects.

CNTs own an outstanding thermal properties, including specific heat and thermal conductivity that determined primarily by phonons (Popov, 2004). Phonon has a similar characteristic as photon, but it exists as a quantum acoustic energy. Phonons are the result of lattice vibrational motions observed in Raman spectra (Vostrowsky, 1997). The information for the type of carriers and conductivity mechanisms can be obtained from the measurements of thermoelectric power of CNTs.

The superlative mechanical properties of CNTs are due to the sp^2 bonding in CNTs (Popov, 2004). Graphite is known to have an in-plane modulus of 1.06 TPa (Chung, 1983). CNTs are expected to display high stiffness and axial strength which is similarly to graphite (Popov, 2004; Ruof and Lorents, 1995). Thoteson et al. (2001) reported that CNTs have an elastic modulus of greater than 1 TPa and strengths of 10–100 times higher than the strongest steel at a fraction of the weight. Besides, CNTs have the highest Young's modulus among other types of composite tubes such as boron nitride, boron carbide, boron carbonitrides and carbon nitride (Salvetat-Delmotte and Rubio, 2002). The physical properties of CNTs are

summarized in Table 2.1.

Table 2.1. Physical properties of the CNTs (Ajayan et al., 2003; Li and Chou, 2003; Li et al., 2005; Lu, 1997; Ma et al., 2008; O'Connell, 2006; Wei et al., 2009; Yu et al., 2000)

Physical Properties	**SWCNTs**	**DWCNTs**	**MWCNTs**
Diameter, nm	1	~ 5	~ 20
Density, g/cm^3	1.3 – 1.5	1.5	1.8 – 2.0
Elastic modulus, TPa	~ 1	~ 1-	0.3 - 1.0
Tensile strength, GPa	50 - 500	23 - 63	10 - 60
Elongation at break (%)	5.8	2.8	1.5 – 4.9
Electrical conductivity, S/cm	~ 10^6		
Thermal stability, ^oC	700 (air)		
Specific surface area, m^2/g	10 - 20		

2.4 Purification of the CNTs

A purification process of the as-prepared CNTs is necessary in order to have a detailed study on their properties and also for their potential applications (Bendjemil et al., 2004; Tan et al., 2008). The CNTs purification method can be classified into three categories: (i) physical, (ii) chemical or (iii) combined physical and chemical method (Hou et al., 2008). Different purification steps can be used depending on the source of the starting material and on the extent of purification needed.

The purification of CNTs by chemical method is based on the selective oxidation process, where carbonaceous particles are easier to be oxidized than CNTs. On the other hand, the metal impurities are easily dissolved in acid solutions. Chemical method has often been used for CNTs purification due to their capability to

remove both metal catalysts and amorphous carbons, except for those encapsulated in polyhedral graphitic particles (Hou et al., 2008). This method can also be applied to purify large quantities of CNTs. However, they tend to destroy the structure of the CNTs by creating functional groups on the sidewalls of CNTs (Park et al., 2006b).

The physical method applied to the purification of the CNTs is based on the differences of the physical properties (physical size, aspect ratio, gravity, magnetic properties and others) between the CNTs and impurities. This method is commonly used to remove undesired carbonaceous particles and graphitic sheets or even separate CNTs that consisted of different physical sizes (Hou et al., 2008). This method does not create damages on CNTs sidewall or changes on their surface properties since no oxidation process is involved (Park et al., 2006b). However, they are rather complicated, time-consuming and less effective than chemical method.

The combined method is the combination of the advantages of physical and chemical methods. This method is used to produce high yield and good quality CNTs. However, a suitable combination of different purification techniques is required to obtain CNTs with the desired properties (Hou et al., 2008). The common purification methods were arranged accordingly in a flowchart, as given in Figure 2.2.

Chemical methods, liquid phase oxidation (LPO) (Colomer et al., 1999; Hernadi et al., 2001; Wang et al., 2006; Yunjin et al., 2008) and gas phase oxidation (GPO) (Chiang et al., 2001; Delpeux et al., 2005; Tobias et al., 2006) have been widely implemented as the methods for CNTs purification method due to their practicality, relative simplicity, and applicability to metal catalysts, catalyst supports and amorphous carbon.

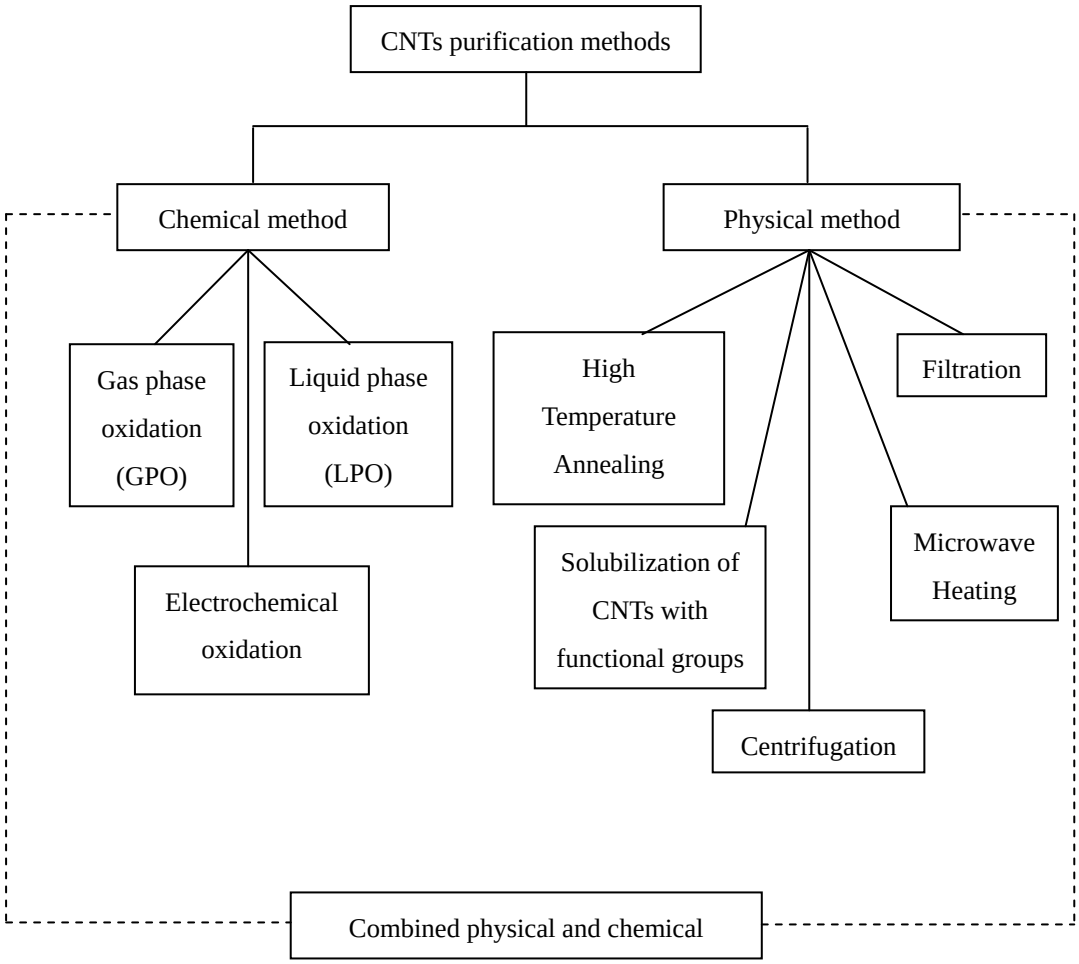


Figure 2.2. CNTs purification methods

LPO has been specifically developed to remove amorphous carbon and metal catalyst. Hou et al. (2008) stated that the selection of oxidant type and precise control of the treatment condition can produce high-purity CNTs in a high yield. This is due to the fact that the oxidative ions and acid ions dissolved in solution can evenly attack the network of raw CNTs. The common oxidants for LPO are nitric acid (HNO_3) (Chen et al., 2002; Dujardin et al., 1998; Hu et al., 2003; Kajiura et al., 2002; Mirershadi et al., 2009; Mohanapriya and Lakshminarayanan, 2007; Shirazi et al., 2011; Wang et al., 2006; Yu et al., 2004; Zhao et al., 2006a), hydrofluoric acid (HF) (Colomer et al., 1999; Hernadi et al., 2001; Yunjin et al., 2008), hydrogen

peroxide (H_2O_2) (Hernadi et al., 2001; Suzuki et al., 2007), and hydrochloric acid (HCl) (Chen et al., 2002; Chiang et al., 2001; Louis et al., 2005; Mackeyev et al., 2007; Shirazi et al., 2011; Song and Fang, 2007; Suzuki et al., 2008; Tohji et al., 1996; Yunjin et al., 2008), mixture of sulphuric acid (H_2SO_4) and HNO_3 (Porro et al., 2007; Shirazi et al., 2011; Wang et al., 2006; Yu et al., 2004), mixture of HNO_3 and HCl (Fan et al., 2006), mixture of H_2O_2 and H_2SO_4 (piranha solution) (Wang et al., 2006), potassium permanganate ($KMnO_4$) (Colomer et al., 1999; Hernadi et al., 2001), potassium hydroxide (KOH) (Louis et al., 2005), and sodium hydroxide (NaOH) (Qiu et al., 2005; Zhao et al., 2006a).

HNO_3 is commonly used to purify MWCNTs by dissolving the metal catalysts and selectively removing the amorphous carbon. However, the inappropriate concentration of HNO_3 and unsuitable reaction time destroyed the CNTs to form carbonaceous particles (Hu et al., 2003). H_2O_2 treatment is applied on the purification of CNTs in order to remove the amorphous carbon but it cannot remove the metal catalysts (Zhao et al., 2006b). The HCl can effectively dissolve the metal catalysts in the CNTs but it failed to remove amorphous carbon (Shirazi et al., 2011).

A mixture of H_2O_2 and HCl was used to overcome the limitation of the H_2O_2 and HCl treatment, respectively (Suzuki et al., 2008; Wang et al., 2006). On the other hand, mixture of HNO_3 and H_2SO_4 was found to produce the CNTs with lesser impurities than HNO_3 treatment (Yu et al., 2004). In addition, CNTs were cut into short, open-ended and carboxylic groups were created at their walls and open ends (Liu et al., 1998; Porro et al., 2007). It was also found that the CNTs structure was damaged when a mixture of HNO_3 and H_2SO_4 was used for purification (Shirazi et al., 2011). Purification of CNTs performed by piranha solution showed lesser oxygen

content and defects on the graphitic surface ends than those purified by HNO_3 (Datsyuk et al., 2008). However, the length of CNTs were reduced and CNTs sidewall damages were created after piranha solution treatment (Wang et al., 2006).

LPO able to remove the impurities in the large scale of CNTs purification and it is also expected to be widely applied for industrial uses in the future. The functional groups formed at the CNTs sidewalls and open ends due to LPO process increase the dispersibility and the solubility of CNTs in most polymers, thus broaden the CNTs practical applications.

GPO was developed mainly to remove the amorphous carbon and carbonaceous particles. Hou et al. (2008) stated that impurities, such as carbonaceous particles can be oxidized in the range of temperature 225^{o}C to 760^{o}C. The common oxidants for GPO are air (Chen et al., 2002; Kajiura et al., 2002; Mohanapriya and Lakshminarayanan, 2007; Shirazi et al., 2011; Song and Fang, 2007; Yu et al., 2004; Yunjin et al., 2008), oxygen gas (Engel-Herbert et al., 2007; Mirershadi et al., 2009), CO_2 (Delpeux et al., 2005), ammonia gas (Wang et al., 2006), hydrogen gas (Vivekchand et al., 2004), steam (Tobias et al., 2006), mixture of argon and oxygen gas (Chiang et al., 2001), and mixture of argon, oxygen gas and steam (Park et al., 2001).

High temperature oxidation in the presence of air is used to purify the as-prepared CNTs. The carbonaceous particles were removed with minor sidewall defects created on the CNTs. However, the yield of pure CNTs was limited due to the uneven exposure of CNTs to the oxidant during GPO and the oxidation selectivity between CNTs and carbonaceous particles.

The quartz tube that placed with CNTs was rotated to allow homogeneously contact between air and CNTs (Park et al., 2001). Song and Fang (2007) applied controllable flux to well mixed the CNTs powders with air in fluidized-bed reactor in order to remove carbonaceous particles. Tan et al. (2008) mixed the CNTs with zirconia beads to increase air flow uniformity and exposure of the CNTs to the air. These methods increased the yield of pure CNTs by allowing CNTs to evenly expose to air.

The other route to improve the yield of pure CNTs for GPO is the enhancement of the difference oxidation resistances between CNTs and carbonaceous particles to air. Chen et al. (1996) reported the brominated CNTs was found to be easily purified than those CNTs without undergoing bromination. The bromination process resulted in a better quality of CNTs, thus enhance their resistances to oxidation. Zimmerman et al. (2000) purified CNTs via a mixture of water, HCl and Cl_2 gas. The Cl_2 in the mixture form the hydroxy-chloride-functional groups on the CNTs caps. Moreover, the HCl gas protected the caps that are more reactive, by preventing the hydroxyl groups from deprotonation. However, the toxicity of the reagents limited its potential use and only small quantities of CNTs were purified by using these reagents.

Chiang et al. (2001) reported that a two-step oxidative cracking could provide better removal of metals. The metal catalysts were found to be able to catalyze the low-temperature oxidation of the carbon. The carbonaceous shells encapsulating metal particles were cracked by Ar/O_2 oxidation, followed by HCl treatment to remove metal catalysts. However, CNTs are hardly purified in large scale due to the complicated steps of a purification method.

GPO is a simple method used to purify the CNTs, which are free of metal catalysts and catalysts support. However, acid treatment is needed as an extra reagent to purify the CNTs containing metal catalysts and catalysts support. Besides, GPO can be combined with other physical methods in order to further improve the purification efficiency.

2.5 Hazardous of the CNTs

CNTs could pose an occupational inhalation exposure hazard since they may enter the working environment as suspended particulate matter of respirable sizes (Lam et al., 2006). The toxicity of the CNTs has raised the high concern in the society due to its similarities to asbestos in term of shape and size, which may lead to lung cancer (Donaldson et al., 2006).

Some animal and cellular studies conducted by Poland et al. (2008) showed that CNTs can cause toxic responses, such as elicit pathological changes in the lungs and other cardiopulmonary diseases. In addition, CNTs are practically insoluble and non-biodegradable fibers (Qiu et al., 2008; Zhang et al., 2005). This will result in environmental pollution as well.

The risk of CNTs had become worse due to the expanding production and widespread application of CNTs (Lim et al., 2011). World production capacity for MWCNTs exceeded 390 tons in 2008, reached 1,500 tons in 2009. Besides, global production for MWCNTs in year 2015 is projected to reach 9,400 tons. (iRAP, 2011)

This may lead to a situation whereby the world would be threatened by the potential hazard and environmental pollution of CNTs. Due to the toxicity of the CNTs and their potential sustainability, thus 3R conceptual idea (reuse, reduce and recycle) could be implemented to overcome the problem.